

THERMAL BEHAVIOUR OF CARBOXYLIC ACID FUNCTIONALITY IN COAL

Tetsuo Aida, Noriyosi Hiram and Yukinari Tsutsumi
Department of Industrial Chemistry
Faculty of Engineering, Kinki University at Kyusyu
11-6 Kayanomori, Iizuka, Fukuoka 820, JAPAN

Keywords: Coal, carboxylic acid functionality, thermal decomposition

INTRODUCTION

Coal contains various chemical functionalities. Among them, the oxygen-containing functionalities are considered to play very important role to control its physical and chemical properties. Particularly, a carboxylic acid functionality has a relatively strong acidic characteristic comparing with other functionalities such as alcoholic and phenolic hydroxyl functionalities, so that it can make strong cohesive forces with a hydrogen bonding to other functionalities bearing electron negative atoms such as oxygen, nitrogen and sulfur. This means that the solubility of coal extracts for various solvents must be greatly affected by its concentration, as well as the apparent cross-linked structure formation in coal by molecular interactions such as hydrogen bonding, charge-transfer bonding or π - π -bonding.

Nevertheless, it has long been a kind of common-sense in the coal science community that the bonding contribution from a carboxylic acid functionality to the chemical and physical property of coal could be negligible toward higher ranked coals like a subbituminous and a bituminous coals. Simply because the previously reported analytical data concerning a carboxylic acid functionality content was too small, which used to be determined by the chemical method developed by Blom et al.(1) about 40 years ago. Although the recent development of sophisticated instrumentalations such as FT-ir, ^{13}C -CP-MAS-NMR, XPS, etc., has made it possible to provide quite reliable informations about such hetero-atom-functionalities as sulfur-, nitrogen- and oxygen-containing functionalities, they seem to have a common problem in the accuracy to determining a small amount of functionality.

At the recent ACS Meeting, we had asked a following question in public with our experimental data obtained by newly developed chemical method(2). However, the low public attention had made us very disappointed.

"Is it true that a bituminous coal contain such a small amount of carboxylic acid functionality in the macromolecular network structure as shown in the Shinn's model(3)(one unit over 660 carbon skeleton) ??".

In Figure 1, our experimental data determined by the new method are summarized. It is just amazing and unbelievable that a wide range of high ranked coals still have a significant amount of carboxylic acid functionality in their macromolecular network structures. Based on these experimental results, Illinois No.6 coal contains at least 6units of carboxylic acid functionality over 660 carbon skeleton which means 6 times more than the Shinn's Model. Furthermore in the case of its pyridine extract, it reached upto 8units/660-carbon. Thus, the conclusion in our previous paper was that there was a possibility of very serious misleading preconception concerning the carboxylic acid functionality in coal, particularly to the higher ranked coals.

Actually, as Niksa pointed out in his recent personal communication and paper(4), it was well-known contradiction that the most of the CO_2 -release during the pyrolyses of subbituminous and bituminous coals could not rationalize by the unimolecular decomposition chemistry of carboxylic acid functionality in coals, because the previously reported quantity of the functionality was too small to use.

This is the strategical background for us to initiate the study on the thermal behaviour of carboxylic acid functionality in coal by means of the direct chemical determination.

EXPERIMENTAL

The chemical reagents were commercial products(Aldrich's gold label grade) which were used without further purifications. Pyridine for the chemical determination of carboxylic acid functionality was dried over calcium hydride and distilled before use. Coals from the Argonne National Laboratory(premium), the Ames Coal Library and BRAIN-C(5) were ground, seized, dried in a silica-gel desiccator at room temperature under vacuum for three days, and stored under a dry nitrogen atmosphere. The thermal treatment of coals(their analytical data shown in Table 1) and model compounds were carried out by using a thick-wall Pyrex glass sealed tubing of which inside atmosphere was replaced by an argon gas, and heated in a molten salt bath for 30 minutes at an appropriate temperature. After the reaction, the sealed tube was cooled down at a liquid nitrogen temperature, and then broken the seal for analyses.

The principle of our chemical determination method of carboxylic acid functionality is described as follows: The chemical reaction with tetra-n-butylammonium borohydrides was adopted for the determination of the carboxylic acid functionality as shown below. Since this reaction proceeds toward different hydroxyl functionalities with very different reaction rates, we can easily discriminate the carboxylic acid functionality from others. The detailed experimental procedure is available in our previous paper(2).



in pyridine solvent
(R = Aryl, Alkyl)

RESULTS AND DISCUSSION

1. Thermal stability of carboxylic acid functionality in coals

In order to examine the thermal stability of carboxylic acid functionality in coals, we have chosen two young coals (Yallourn, Dietz No.1&2) and two relatively old coals (Illinois No.6, Pittsburgh No.8). These coals were carefully handled under a nitrogen atmosphere to prevent an auto-oxidation by air, and also the heat-denaturation for which the drying operation was performed by using a silica-gel vacuum desiccator at room temperature for three days.

In Figure 2, the degree of the decomposition of the carboxylic acid functionality in each coals for 30 minutes were demonstrated versus temperatures.

Very interestingly, the pattern of the decomposition seems to be quite different between these two groups, that is, the carboxylic acid functionalities in the old coals were relatively stable below 350°C, and started to decompose over 400°C, meanwhile the young coals seemed to contain significant amount of reactive(unsafe?) carboxylic acid functionality. Almost 40% of carboxylic acid functionality in coal destroyed under 300°C within 30 minutes heating condition. These results are consistent with a general understanding of a coalification process which is considered to predominantly destroy the reactive functionality in coal. Based on this assumption, the thermal decomposition pattern of the old coal, i.e., Pittsburgh No.8 coal, represents that of the stable form of carboxylic acid functionality in coal. Namely, the decomposition rate is accelerated over 400°C, and about 80% of the total content can be destroyed within 30 minutes at 450°C.

Meanwhile, in the case of the young coals (Lignite) the total content of carboxylic acid functionality are 2-3 times more than those of the old coals, and the most of the functionalities are reactive form which can be decomposed below 400°C. Obviously, the thermal decomposition pattern around 450°C suggest that some amount of stable form of functionality exists in the coal. It is also interesting that the fine structure of the decomposition pattern appeared between 200°C to 350°C suggests that the reactive functional group consisted from further different groups of the functionalities. Although at this moment it will be too early to draw a conclusion, there seems to be interesting coincidence between our data and the CO₂-release rate of the coal pyrolysis reported by Solomon, et al. (6) shown in Figure 3. We have not yet enough stoichiometric data concerning the decomposition of carboxylic acid functionality and the amount of the released CO₂ during the pyrolyses. But, it is quite plausible that the yield of CO₂ in the coal pyrolysis can be rationalized in terms of unimolecular decomposition chemistry of carboxylic acid functionality.

2. Thermal stabilities of model compounds

It has been found that coal contained several groups of carboxylic acid functionalities which had a different thermal stability. So, we have decided to assume the chemical structure of the functionality by comparing with those of the structure-known model compounds.

The first group of the model compounds chosen are the simple aromatic and aliphatic carboxylic acid compounds such as toluic acid, 1- and 2-naphthoic acid, and n-hexanoic acid which are assumed to be thermally quite stable.

Figure 4, summarized the experimental data obtained under the same reaction conditions as used for the coals, previously. The thermal decomposition patterns of the aromatic carboxylic acid, i.e., toluic acid, 1-and 2-naphthol seemed to be quite similar to those of higher ranked coals (Figure 2). The thermal stability of the alkyl derivative seems to be quite stable compared to others, which was decomposed over 450°C.

All of these results strongly suggest that the major component of carboxylic acid functionality in the old coal such as Illinois No.6 and Pittsburgh No.8 coals, must be simple aromatic and/or aliphatic derivatives. This assumption seems to be consistent with our previous understanding, for example, Shinn's model adopted a single aromatic carboxylic acid functionality.

The second group of the model compounds chosen are mainly the nature-oriented form of carboxylic acid compounds such as malic acid and fumaric acid, of which existence in coal are not sure, but it is considered to be one of the candidates for the possible functionality in younger coals like a lignite.

The results obtained are summarized in Figure 5.

As expected, these model compounds started to decompose under relatively mild conditions, around 250-300°C.

Of course it is quite difficult to assume with these data that the actual chemical structure of the reactive carboxylic acid functionality in coals are just like these chemical structure. But at least, we may be able to say that the younger coals like a lignite have much of a nature-oriented (raw) form of carboxylic acid functionality in the macromolecular network structure. Also, the carboxylic acid functionality of which chemical reactivity can be significantly enhanced by the specific substituents or hetero-atoms like a 9-anthracenecarboxylic acid seems to be responsible for such a mild decompositions.

CONCLUSION

It was found that the coal contains both stable form and relatively unstable form of carboxylic acid groups in the macromolecular network structure. The former seem to be a simple aromatic carboxylic acid, and the later is assumed to be more natural product like carboxylic acid functionality. It is also likely that the previous observation of the CO₂-release during the pyrolyses of coals can be rationalized by the unimolecular decomposition chemistry of carboxylic acid functionality in coal.

ACKNOWLEDGEMENTS

A part of this research was supported by the grant from The Japanese Ministry of Education through The Nippon Gakujutu Shin-koukai.

REFERENCES

- (1) Blom, L., Edelhausen, L., and van Krevelen, D.W., *Fuel*, **36**, 135(1957)
- (2) Aida, T, et al., *Prepr. Am. Chem. Soc. Div. Fuel Chem.*, **41**(2), 744(1996)
- (3) Shinn, J.H., *Fuel*, **63**, 1187(1984)
- (4) Niksa, Stephen, *Energy & Fuels*, **10**, 173(1996)
- (5) Coal Bank sponsored by NEDO through CCUJ(Japan)
- (6) Solomon, P. R., et al., *Energy & Fuels*, **4**, 319(1990)

Table 1. Analytical Data of Coals

Coal	(dmmf wt %)					(mmol / g)		
	Ash	C	H	N	O	S	COOH	Ph-OH
Yallourn*	1.6	66.9	4.70	0.48	27.7	0.26	1.28	4.61
Dietz No.1 & 2	5.5	74.4	5.26	1.09	18.9	0.44	1.27	-
Illinois No.6**	14.3	80.7	5.20	1.43	10.1	4.82	0.67	2.52
Pittsburgh No.8**	9.1	85.0	5.43	1.68	6.90	2.19	0.37	2.04

* Australian brown coal

** Argonne premium coal

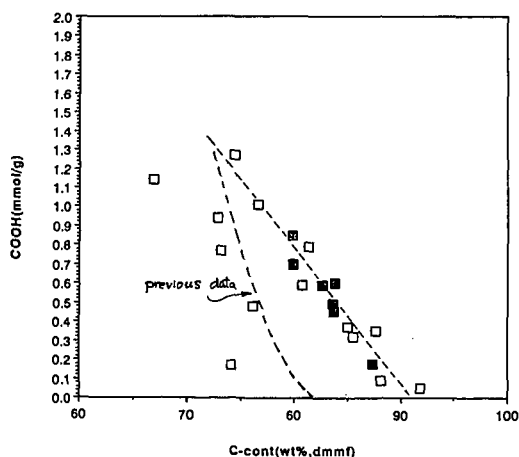


Figure 1. Coal rank dependency of Carboxylic acid functionality content

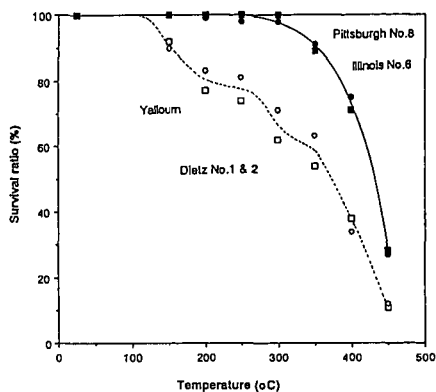


Figure 2. Thermal stabilities of carboxylic acid functionality in coals

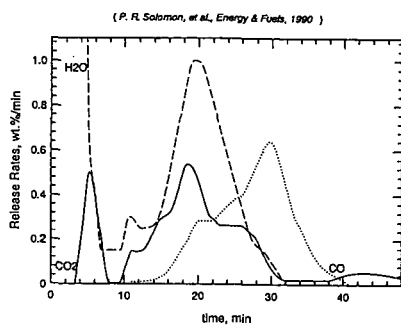


Figure 3. Release rates of gaseous products from thermal decomposition of subbituminous coal (6)

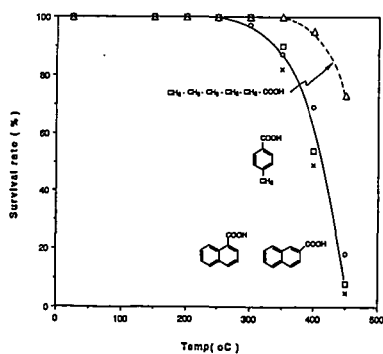


Figure 4. Thermal stabilities of model compounds

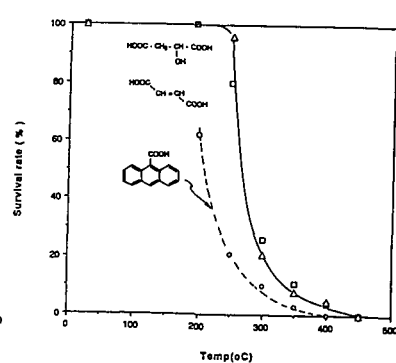


Figure 5. Thermal stabilities of model compounds